(54) Title: METHOD OF DRY ETCHING, DRY ETCHING GAS AND PROCESS FOR PRODUCING PERFLUORO-2-PENTYNE

(54) 発明の名称: ドライエッチング方法、ドライエッチングガスおよびパーフルオロ−2−ペンチンの製造方法

(57) Abstract: A method of dry etching, comprising exposing a resist film to radiation of 195 nm or less wavelength so as to form a resist pattern of 200 nm or less minimum line width and subjecting the resist pattern to dry etching using a fluorinated compound of C_4-C_6 having at least one unsaturated bond as an etching gas. Perfluoro-2-pentyne, perfluoro-2-butyne, nonafluoro-2-pentene and perfluoro-2-pentene are preferably used as the fluorinated compound. Perfluoro-2-pentyne can be synthesized by reacting a 1,1,1-trihalo-2,2,2-trifluoroethane with pentafluoropropylene aldehyde into a 2-halo-1,1,1,4,4,5,5,5-octafluoro-2-pentene and eliminating a hydrogen halide from this 2-pentene.

(57) 要約: レジスト膜に波長が 1 9 5 n m 以下の放射線を照射して最小線幅 2 0 0 n m 以下のレジストパターンを形成し、次いで、エッチングガスとして少なくとも 1 つの不飽和結合を有する炭素数 4 〜 6 のフッ素系化合物を用いて該レジストパターンをドライエッチングすることからなるドライエッチング方法。該フッ素系化合物としては、パーフルオロ−2−ペンチン、パーフルオロ−2−ブチン、ノナフルオロ−2−ペンテン、ノナフルオロ−2−ペンテンおよびパーフルオロ−2−ペンテンが好ましく用いられる。パーフルオロ−2−ペンチンは、 1, 1, 1−トリハロ−2, 2, 2−トリフルオロエタンとペンタフルオロプロピオンアルデヒドを反応させて 2−ハロ−1, 1, 1, 4, 4, 5, 5, 5−オクタフルオロ−2−ペンテンとし、次いで、該 2−ペンテンを脱ハロゲン化水素することにより合成される。

WO 2004/008515 A1

DESCRIPTION

Method of Dry Etching, Dry Etching Gas and Process for Producing Perfluoro-2-pentyne

Technical Field

This invention relates to a method of dry etching, a dry etching gas, and a process for producing perfluoro-2-pentyne. More particularly, this invention relates to a method of dry etching wherein an etching rate is high, a selectivity for substrate is high, and a fine pattern having a minimum line width of not more than 200 nm can be formed on a silicon substrate at an enhanced stability; a dry etching gas; and a process for producing perfluoro-2-pentyne used for the dry etching.

Background Art

With the advance in high integration and high performance of integrated circuits of semiconductor devices such as VLSI (very large scale integrated circuit) and ULSI (ultra large scale integrated circuit) in recent years, technical demands for a dry etching gas used in the production process of these semiconductor devices are becoming increasingly strict. As the dry etching gas, saturated fluorocarbon gases such as carbon tetrafluoride and perfluorocyclobutane have heretofore been widely used. However, it is said that saturated fluorocarbon gases have a long life in the air, namely, a life of several-thousands years, and exert a considerable influence upon the global warming. Therefore, various fluorine-containing compounds have been developed as alternatives for saturated fluorocarbon gases.

Fluorine-containing compounds having an unsaturated bond are disclosed in Japanese Unexamined Patent Publication H9-191002. It is reported in this patent publication that evaluation of etching was conducted on a resist pattern formed with radiation having a wavelength of 300 nm by a KrF excima laser lithography, and good results were obtained. In Japanese Unexamined Patent Publication 2002-184768, it is reported that evaluation of etching was

conducted on a resist pattern formed by lithography using deep UV, namely, ultraviolet rays of a wavelength of 200 to 300 nm, and good results were obtained.

For the exposure to radiation with a wavelength of at least 200 nm, for example, irradiation using a KrF with a wavelength of 248 nm, a resist formed from a high molecular weight compound having an aromatic ring structure has heretofore been widely used. This is because a resist formed from a high molecular weight compound having an aromatic ring structure exhibits a high resistance for dry etching, and, at an etching step after light exposure and development, a high etching selectivity for silicon oxide substrate can be obtained. However, a resist pattern having a minimum line width of 210 nm can be obtained at the utmost with a KrF (248 nm) excima laser used for 256 megabit DRAM. With further advance in integration of integrated circuits in a semiconductor device, an ArF (193 nm) excima laser or other light sources of shorter wavelength should be used for the production of DRAM with 1 gigabit or more. However, in the case where a high molecular weight compound having an aromatic ring structure is used, a fine pattern cannot be formed when radiation with a wavelength of 200 nm or less such as ArF (193 nm) laser or X-rays is used, because radiation is absorbed to an undue extent by an aromatic ring.

Now high molecular weight compounds having an alicyclic structure and alkali-soluble methacrylic acid copolymers are being examined for the formation of a resist for radiation with a wavelength of 195 nm or less such as ArF and X-rays. However, these high molecular weight compounds do not contain or contain only a minor proportion of an aromatic ring structure, and therefore, a problem arises at an etching step after light exposure and development, in that an unexposed area of resist tends to be undesirably etched depending upon the particular kind of etching gas, and thus, the etching selectivity for silicon oxide is low. For example, in the case when perfluoropropene, which is said to be useful for a resist for radiation with a wavelength of more than 195 nm, is used for dry etching of a silicon oxide film, a protective coating such as polysilicon as well as an unexposed area of a

photoresist tend to be undesirably etched, and thus, the etching selectivity for silicon oxide is not high and a fine pattern is difficult to form.

Especially, with a great reduction in line width of a resist pattern, for example, in the order of 200, 180, 130 and 100 nm, a resist formed on a substrate represented by silicon oxide film becomes thinner, and therefore, a high etching selectivity becomes more difficult to attain.

Disclosure of the Invention

An object of the present invention is to provide a method of dry etching by which a high etching rate and a high etching selectivity can be attained and a fine resist pattern with a minimum line width of 200 nm or less can be formed with good stability, even for a resist having poor resistance to dry etching using a light source with a short wavelength of 195 nm or less.

Another object of the present invention is to provide a dry etching gas by which a high etching rate and a high etching selectivity can be attained and a fine resist pattern with a minimum line width of 200 nm or less can be formed with good stability, even for a resist having poor resistance to dry etching using a light source with a short wavelength of 195 nm or less.

A further object of the present invention is to provide a process for producing perfluoro-2-pentyne which is suitable for use as the above-mentioned dry etching gas.

The inventors made an extensive research for achieving the above-mentioned objects, and found that, in the case when dry etching is carried out using a fluorine-containing compound having 4 to 6 carbon atoms and at least one unsaturated bond as an etching gas, a high etching selectivity can be attained without reduction of etching rate, even for a resist having poor resistance to dry etching. Based on this finding, the present invention has been completed.

Thus, in one aspect of the present invention, there is provided a dry etching method characterized in that a resist film formed on a substrate is irradiated with radiation having a

wavelength of not more than 195 nm to form a resist pattern having a minimum line width of not more than 200 nm, and the substrate having the resist pattern formed thereon is subjected to dry etching using a fluorine-containing compound having 4 to 6 carbon atoms and at least one unsaturated bond as an etching gas.

In another aspect of the present invention, there is provided a dry etching gas comprised of a fluorine-containing compound having 4 to 6 carbon atoms and at least one unsaturated bond, and used for dry etching for a resist film forming a resist pattern having a minimum line width of not more than 200 nm at irradiation with radiation having a wavelength of not more than 195 nm.

In a further aspect of the present invention, there is provided a process for producing perfluoro-2-pentyne characterized in that a 1,1,1-trihalo-2,2,2-trifluoroethane is allowed to react with pentafluoropropionaldehyde to give a 2-halo-1,1,1,4,4,5,5,5-octafluoro-2-pentene, and the thus-produced 2-halo-1,1,1,4,4,5,5,5-octafluoro-2-pentene is dehydrohalogenated.

Best Mode for Carrying Out the Invention

In the dry etching method of the present invention, a resist film formed on a substrate is irradiated with radiation having a wavelength of not more than 195 nm to form a resist pattern having a minimum line width of not more than 200 nm, and then, the substrate having the resist pattern thus-formed thereon is subjected to dry etching using a fluorine-containing compound having 4 to 6 carbon atoms and at least one unsaturated bond as an etching gas. By this method, the etching of a substrate can be effectively carried out and thus, a fine pattern of a minimum line width of not more than 200 nm, preferably not more than 180 nm, more preferably not more than 150 nm and especially preferably not more than 140 nm can be easily formed with a high precision. By the term "minimum line width" as used herein, we mean broadly those which include, for example, a diameter of contact holes in the case when the resist pattern is contact holes.

If a fluorine-containing compound having at least one unsaturated bond, but having three or less carbon atoms, is used

as a dry etching gas, the selectivity in dry etching tends to be reduced. A fluorine-containing compound having at least one unsaturated bond but having at least 7 carbon atoms is usually difficult to use as a dry etching because it has a high boiling point.

The resist film formed on a substrate is not particularly limited, but is preferably formed from a high molecular weight compound containing 0% to 10% by weight of repeating units having an aromatic ring structure. The content of repeating units having an aromatic ring structure in the high molecular weight compound constituting the resist film is more preferably in the range of 0% to 5% by weight, especially 0% to 2% by weight. When the content of repeating units having an aromatic ring structure in the high molecular weight compound constituting the resist film is in the range of 0% to 10% by weight, transparency to radiation with a wavelength of not more than 195 nm can be obtained and a desired resist pattern having a minimum line width of not more than 200 nm can be formed.

As specific examples of the high molecular weight compound containing 0% to 10% by weight of repeating units having an aromatic ring structure, there can be mentioned a partially hydrogenated resin product of a p-hydroxystyrene/t-butyl methacrylate copolymer, a partially hydrogenated resin product of a p-hydroxystyrene/-4-ethenylphenoxyacetic acid 1-alkylcyclohexyl ester copolymer, an isobornyl methacrylate/methyl methacrylate/t-butyl methacrylate/methacrylic acid quaternary polymer, an adamantyl methacrylate/t-butyl methacrylate copolymer resin, a valerolactone metacrylic acid ester/2-alkyladamantyl methacrylate/hydroxyadamantyl methacrylate terpolymer resin, a t-butyl methacrylate/vinyl alkyl ether/maleic anhydride terpolymer resin, a norbornenecarboxylic acid/t-butyl norbornenecarboxylate/alkylnorbornene/maleic anhydride quaternary polymer resin, a norbornenecarboxylic acid/t-butyl norbornenecarboxylate/alkylnorbornene terpolymer resin, a hydrogenated product resin of a metathesis ring-open copolymer of an alkyl norbornenecarboxylate with t-butyl

tricyclodecenecarboxylate, and a hydrogenated product resin of a metathesis ring-open copolymer of a norbornene t-butylcarboxylic acid ester with tricyclodecenecarboxylic acid alkyl ester.

The procedure for forming a resist film on a substrate is not particularly limited and the conventional procedure may be adopted. For example, a solution of a resist composition is applied onto a substrate by spin coating or other coating means, and then a solvent is removed by evaporation from the coating solution to be thereby dried. According to the need, the dried coating is pre-baked. In the solution of a resist composition, an acid generator such as an onium salt, diazomethane derivatives and glyoxime derivatives can be incorporated according to the need.

The radiation used in the present invention has a wavelength of not more than 195 nm, preferably not more than 170 nm especially preferably not more than 150 nm. The radiation is not particularly limited provided that it has a wavelength of not more than 195 nm. As specific examples of the radiation used, there can be mentioned ArF excima laser (193 nm), F_2 excima laser (157 nm), Kr_2 excima laser (146 nm), KrAr excima laser (134 nm), AR_2 excima laser (126 nm), vacuum ultraviolet rays (not more than 170 nm), electron beam (EB) and X rays.

The procedure for forming a resist pattern is also not particularly limited. For example, a resist film is masked and irradiated with radiation according to the pattern. Then the irradiated resist is post-baked according to the need, and development is carried out using an aqueous alkali such as an aqueous tetramethylammonium hydroxide solution to form a resist pattern, followed by dry etching.

In the dry etching method of the present invention, a fluorine-containing compound having 4 to 6 carbon atoms and at least one unsaturated bond is used as a dry etching gas. By the term "fluorine-containing compound" as used herein, we mean a compound composed of carbon and fluorine or a compound composed of carbon, hydrogen and fluorine. The unsaturated bond may be either a double bond or a triple bond. The fluorine-containing compound may have both a double bond and a triple bond.

As specific examples of the fluorine-containing compound having a triple bond, there can be mentioned perfuoro-1-butyne, perfuoro-2-butyne, perfuoro-1-pentyne, perfuoro-2-pentyne, perfuoro-1,3-pentadiyne, perfuoro-1,4-pentadiyne, perfuoro-1-hexyne, perfuoro-2-hexyne, perfuoro-3-hexyne, perfuoro-1,3-hexadiyne, perfuoro-1,4-hexadiyne, perfuoro-1,5-hexadiyne and perfuoro-2,4-hexadiyne.

As specific examples of the fluorine-containing compound having a double bond, there can be mentioned perfuoro-1-butene, perfuoro-2-butene, perfuoro-1,3-butadiene, perfuoro-1-pentene, perfuoro-2-pentene, perfuoro-1,3-pentadiene, perfuoro-1,4-pentadiene, perfuoro-2-methyl-1,3-butadiene, octafluorocyclopentene, hexafluorocyclopentadiene, perfluoro-1-hexene, perfluoro-2-hexene, perfluoro-3-hexene, perfluoro-1,3-hexadiene, perfluoro-1,4-hexadiene, perfluoro-1,5-hexadiene, perfluoro-2,4-hexadiene, perfluoro-1,3,5-hexatriene, perfluoro-1,3-cyclohexadiene, perfluoro-1,4-cyclohexadiene, perfluorobenzene, 1,1,1,2,4,4,4-heptafluoro-2-butene, 1,3,3,4,4-pentafluorocyclobutene, 1,2,3,4,4-pentafluoro-cyclobutene, 1,1,1,2,4,4,5,5,5-nonafluoro-2-pentene, 1,1,1,3,4,4,5,5,5-nonafluoro-2-pentene, 1,1,1,2,3,4,5,5,5-nonafluoro-2-pentene, 1,3,3,4,4,5,5-heptafluorocyclopentene, 1,2,3,4,4,5,5-heptafluorocyclopentene, 1,2,3,3,4,5,5-heptafluorocyclopentene, 1,1,1,3,4,4,5,5,6,6,6-undecafluoro-2-hexene, 1,1,1,2,4,4,5,5,6,6,6-undecafluoro-2-hexene, 1,1,1,2,2,4,5,5,6,6,6-undecafluoro-3-hexene and 1,1,1,2,2,3,5,5,6,6,6-undecafluoro-3-hexene.

As specific examples of the fluorine-containing compound having both of a double bond and a triple bond, there can be mentioned perfuoro-1-buten-3-yne, perfuoro-1-penten-3-yne, perfuoro-1-penten-4-yne, perfuoro-3-penten-1-yne, perfuoro-2-methyl-1-buten-3-yne, perfuoro-1-cyclohexen-3-yne and perfuoro-1-cyclohexen-4-yne.

The above-mentioned fluorine-containing compound having at least one unsaturated bond may be used either alone or as a combination of at least two thereof as a dry etching gas. Of the

above-recited fluorine-containing compounds, perfluoro-2-butyne, perfluoro-2-pentyne, perfuoro-2-hexyne, perfluoro-3-hexyne, 1,1,1,2,4,4,5,5,5-nonafluoro-2-pentene, 1,1,1,3,4,4,5,5,5-nonafluoro-2-pentene and perfuoro-2-pentene are preferable because of high stability. 1,1,1,2,4,4,5,5,5-nonafluoro-2-pentene, 1,1,1,3,4,4,5,5,5-nonafluoro-2-pentene and perfuoro-2-pentene are especially preferable. Perfluoro-2-pentyne and perfluoro-2-butyne are preferable in view of high etching rate and high etching selectivity. Perfluoro-2-pentyne is especially preferable.

The fluorine-containing compound having 4 to 6 carbon atoms and at least one unsaturated bond preferably has a purity of at least 90% by volume, more preferably at least 99% by volume and especially preferably at least 99.9% by volume. If the fluorine-containing compound has a purity of lower than 90% by volume, the etching rate and the etching selectivity are liable to be poor.

A material to be etched includes, for example, silicon oxide, silicon nitride, aluminum, tungsten, molybdenum, tantalum, titanium, chromium, chromium oxide and gold. As specific examples of the substrate to be etched, there can be mentioned silicon wafer having silicon oxide film or aluminum film. The size of silicon wafer is not particularly limited, but the silicon wafer usually has a size of 8 inches or 12 inches.

At a dry etching step, etching is carried out preferably under irradiation with a plasma. The plasma preferably has a density of at least 10^{10} ions/cm^3, more preferably in the range of 10^{10} to 10^{13} ions/cm^3. When the plasma density is in the range of 10^{10} to 10^{13} ions/cm^3, higher etching rate and higher etching selectivity can be obtained and a fine pattern can be formed. As examples of an apparatus for generating plasma, there can be mentioned those which are of a helicon wave type, a high-frequency induction type, a parallel flat plate type and a magnetron type. Of these, a helicon wave type apparatus and a high-frequency induction type apparatus are preferable because a plasma having a high density region can be easily generated.

At a dry etching step, the fluorine-containing compound

having 4 to 6 carbon atoms and at least one unsaturated bond is preferably introduced into an apparatus vacuumed to an extent such that the inner pressure reaches a pressure in the range of 0.0013 to 1,300 Pa, more preferably 0.13 to 1.3 Pa. The temperature which the substrate to be dry-etched reaches during the dry etching step is preferably in the range of 0 to 300°C, more preferably 60 to 250°C and especially preferably 80 to 200°C. The treating time for the dry etching is usually in the range of 10 seconds to 10 minutes. However, etching can be effected at a high etching rate in the dry etching method of the present invention, and therefore, the dry etching can be carried out for a treating time of 10 seconds to 3 minutes with a high productivity.

At a dry etching step, other gas can be additionally incorporated in the etching apparatus. The gas used in combination with the fluorine-containing compound includes, for example, rare gases such as helium, neon, argon, krypton and xenon; and oxygen and oxygen-containing gases such as carbon monoxide and carbon dioxide. Of these, oxygen is preferably used in combination with the fluorine-containing compound because oxygen has a dissociation accelerating action for an etching gas.

The dry etching gas used in the present invention is comprised of a fluorine-containing compound having 4 to 6 carbon atoms and at least one unsaturated bond, with which dry etching is carried out for a resist pattern having a minimum line width of not more than 200 nm formed by irradiation with radiation with a wavelength of not more than 195 nm. As the fluorine-containing gas having 4 to 6 carbon atoms, various gases can be used as mentioned above. Perfluoro-2-pentyne is especially preferably used because high etching rate and high etching selectivity can be obtained.

In the process for producing perfluoro-2-pentyne according to the present invention, a 1,1,1-trihalo-2,2,2-trifluoroethane is allowed to react with pentafluoropropionaldehyde to give a 2-halo-1,1,1,4,4,5,5,5-octafluoro-2-pentene, and the thus-produced 2-halo-1,1,1,4,4,5,5,5-octafluoro-2-pentene is dehydrohalogenated to give perfluoro-2-pentyne.

The conditions for allowing a 1,1,1-trihalo-2,2,2-

trifluoroethane to react with pentafluoropropionaldehyde are not particularly limited. For example, pentafluoropropionaldehyde hydrate is treated with a dehydrating agent such as phosphorus pentoxide under heated conditions to be thereby dehydrated to give pentafluoropropionaldehyde, and the pentafluoropropionaldehyde is blown in a cooled polar solvent such as dimethylformamide to give a solution. To the thus-obtained solution, a 1,1,1-trihalo-2,2,2-trifluoroethane and powdery zinc oxide were added, and the mixture is heated to give a 2-halo-1,1,1,4,4,5,5,5-octafluoro-2-pentene. The amount of pentafluoropropionaldehyde hydrate used is preferably in the range of 1 to 2 moles, more preferably 1.2 to 1.5 moles, per mole of a 1,1,1-trihalo-2,2,2-trifluoroethane to be reacted with a dehydrated product of the pentafluoropropionaldehyde hydrate. The amount of powdery zinc added is preferably in the range of 2 to 3 moles, more preferably 2.2 to 2.5 moles, per mole of the 1,1,1-trihalo-2,2,2-trifluoroethane. Powdery zinc oxide is preferably previously activated by treating with, for example, dilute aqueous hydrochloric acid or acetic anhydride prior to the addition to the pentafluoropropionaldehyde solution. A preferable example of the starting material, 1,1,1-trihalo- 2,2,2-trifluoroethane, is 1,1,1-trichloro-2,2,2-trifluoroethane. The reaction temperature is usually in the range of room temperature to 150°C, more preferably 50°C to 100°C. The reaction time is usually in the range of 1 to 20 hours, more preferably 3 to 10 hours.

An after-treatment for the above-mentioned reaction may be conventional. That is, the reaction is stopped by adding dilute hydrochloric acid to the reaction liquid, and the reaction product is extracted with an extract solvent such as ethyl acetate or diethyl ether, neutralized with a saturated aqueous sodium bicarbonate solution, and then dried over a desiccating agent such as sodium sulfate. The dried product is concentrated by a rotary evaporator to give a crude purified product. The crude purified product may be subjected to the dehydrohalogenation, or, may be distilled for purification and then subjected to the dehydrohalogenation.
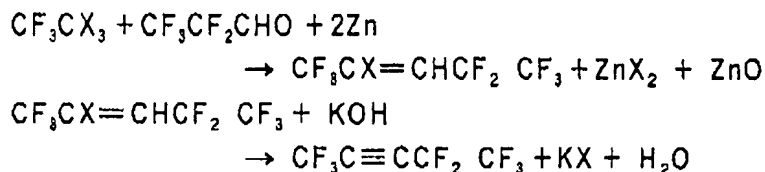
Then a basic compound such as, for example, potassium

hydroxide is added to the obtained 2-halo-1,1,1,4,4,5,5,5-octafluoro-2-pentene whereby dehydrohalogenation is effected to produce a triple bond, namely, give perfluoro-2-pentyne. More specifically, a pressure-resistant autoclave is charged with a basic compound and the 2-halo-1,1,1,4,4,5,5,5-octafluoro-2-pentene, and the content is heated, and a gaseous product produced by the reaction is collected in a cooled trap. Alternatively, a procedure utilizing a feature such that perfluoro-2-pentyne to be produced has a boiling point of 5°C can be adopted. That is, a reactor is previously charged with a basic compound, and, while the content was stirred, the 2-halo-1,1,1,4,4,5,5,5-octafluoro-2-pentene was dropwise added and a gaseous product produced by the reaction is collected in a cooled trap.

The amount of basic compound used is preferably in the range of 1 to 10 moles, more preferably 2 to 5 moles, per mole of the 2-halo-1,1,1,4,4,5,5,5-octafluoro-2-pentene. The reaction temperature is usually in the range of room temperature to 250°C, more preferably 50°C to 200°C.

The collected perfluoro-2-pentyne can be subjected to distillation for enhancing the purity.

The reaction scheme in the above-mentioned production process of the present invention is shown below, wherein X represents halogen selected from chlorine, bromine and iodine.

$$CF_3CX_3 + CF_3CF_2CHO + 2Zn$$
$$\rightarrow CF_3CX{=}CHCF_2CF_3 + ZnX_2 + ZnO$$
$$CF_3CX{=}CHCF_2CF_3 + KOH$$
$$\rightarrow CF_3C{\equiv}CCF_2CF_3 + KX + H_2O$$

According to the process for producing perfluoro-2-pentyne, perfluoro-2-pentyne having a high purity can be produced with an enhanced efficiency from a readily available raw material, as compared with heretofore proposed processes for producing perfluoro-2-pentyne, which include dechlorination of 2,3-dichloro-1,1,1,4,4,5,5,5-octafluoro-2-pentene by using zinc, isomerization of perfluoropentadiene, or dehydrofluorination of 1,1,1,2,3,4,4,5,5,5-decafluoropentane.

Examples

The invention will now be described more specifically by the following working examples that by no means limit the scope of the invention.

In the working examples, parts are by weight unless otherwise specified.

In examples and comparative examples, selectivity ratio in etching was calculated by the following equation.

Selectivity ratio etching = (etching rate for silicon oxide film)/(etching rate for resist)

Production Example 1

An autoclave made of Hastelloy was charged with 394 parts of commercially available palletized potassium hydroxide (purity: 85% by weight) and 300 parts of 1,1,1,2,3,4,4,5,5,5-decafluoropentane ("Vertrel™ XF" available from Du pont). The content was thoroughly stirred and a reaction was carried out at 200°C for 7.5 hours.

The autoclave was cooled, and then, in order for distilling and collecting the thus-produced reaction mixture, a condenser and a vacuum pump were connected to the autoclave. The reaction mixture was collected into the condenser, which was cooled under a reduced pressure by liquid nitrogen, to give 182.5 parts of a reaction product. Analysis of the reaction product by gas chromatography revealed that it contained perfluoro-2-pentyne (target product), 1,1,1,2,4,4,5,5,5-nonafluoro-2-pentene, 1,1,1,3,4,4,5,5,5-nonafluoro-2-pentene and a small amount of 1,1,1,2,3,4,4,5,5,5-decafluoropentane (raw material). The yield of the target product was 20.6% by weight based on the amount of the raw material charged. A great portion of the unreacted raw material was decomposed and polymerized, which remained within the autoclave, and thus, the reaction product contained only about 1% by weight of raw material.

The above-mentioned reaction procedure was repeated to collect the reaction products. 1,202 parts of the collected reaction products (content of perfluoro-2-pentyne: 31.96% by volume) was fractionated under normal pressure by using a KS type fractionating column with a theoretical plate number of 35. A

cooling medium at the top of the fractionating column was maintained at a temperature of -5 to -10°C, and a trap for collecting the desired fraction was maintained at a temperature of -78°C. This fractionation gave 264 parts of a perfluoro-2-pentyne fraction (boiling point: 5°C) having a purity of 99.9% by volume.

Production Example 2

200 parts of commercially available perfluoro-2-butyne (available from SynQuest Laboratories, Inc., purity: 98% by volume) was fractionated by using a pressure distillation column (PMN-2507FF available from Toka Seiki K.K., theoretical plate number: 33) to give 123 parts of perfluoro-2-butyne having a purity of 99.9% by volume and a boiling point of -24°C.

Production Example 3

200 parts of commercially available perfluoro-2-pentene (available from SynQuest Laboratories, Inc., purity: 99% by weight) was fractionated under normal pressure by using a KS type fractionating column with a theoretical plate number of 35. A cooling medium at the top of the fractionating column was maintained at -5 to -10°C and a fraction was collected in a flask cooled by ice water. The fractionation gave 157 parts of perfluoro-2-pentene (boiling point: 26°C) having a purity of 99.9% by weight.

Example 1

Ten parts of a terpolymer comprised of 5-norbornene-2-methanol units, maleic anhydride units and t-butyl methacrylate units (copolymerization ratio: 1:1:1 by mole; molecular weight: 5,500) and 0.2 part of triphenylsulfonium trifluoromethane sulfonate as an acid generator were dissolved in 70 parts of propylene glycol monomethyl ether acetate, and the resulting solution was filtered through a filter having a pore diameter of 100 nm to give a resist solution.

A silicon substrate of an 8 inch diameter having a coating of silicon oxide film with a thickness of 2 μm was coated with the above-mentioned resist solution by a spin-coating procedure, and then, the thus-coated substrate was pre-baked at 120°C on a hot plate to form a resist film having a thickness of 450 nm. The resist film was exposed to light through a mask pattern by an ArF

excima-laser aligner (wavelength: 193 nm). The light-exposed resist film was post-baked at 130°C, and then subjected to a developing treatment at 25°C for 60 seconds with an aqueous solution of tetramethylammonium hydroxide having a concentration of 2.38% by weight, and dried to form contact holes having a diameter of 130 nm.

The thus-obtained substrate having contact holes was set in an ICP plasma etching apparatus. The inside of the apparatus was vacuumed, and perfluoro-2-pentyne as a dry etching gas, produced in Production Example 1, was introduced into the etching apparatus at a rate of 50 sccm. Etching was carried out at a plasma density of 10^{11} ions/cm^3 while the inner pressure was maintained at 0.67 Pa.

The etching rate of the silicon oxide film was 621.0 nm/min at the central portion and 564.1 nm/min at the edge portion. The etching rate of the resist film was 33.6 nm/min at the central portion and 41.5 nm/min at the edge portion. Thus, the selectivity ratio in etching was 18.5 in the central portion and 13.6 at the edge portion.

Example 2

Etching was carried out by the same procedures as those adopted in Example 1 except that perfluoro-2-butyne produced in Production Example 2 was used as a dry etching gas with all other conditions remaining the same. Etching rate and selectivity ratio were evaluated in the same manner as in Example 1.

Example 3

Etching was carried out by the same procedures as those adopted in Example 1 except that perfluoro-2-pentene produced in Production Example 3 was used as a dry etching gas with all other conditions remaining the same. Etching rate and selectivity ratio were evaluated in the same manner as in Example 1.

Example 4

Etching was carried out by the same procedures as those adopted in Example 1 except that perfluoro-1,3-butadiene having a purity of 99.9% by volume, prepared by fractionating commercially available perfluoro-1,3-butadiene (available from SynQuest

Laboratories, Inc.), was used as a dry etching gas with all other
conditions remaining the same. Etching rate and selectivity ratio
were evaluated in the same manner as in Example 1.

Comparative Example 1

Etching was carried out by the same procedures as those
adopted in Example 1 except that perfluoropropene having a purity
of 99.9% by volume, prepared by fractionating commercially
available perfluoropropene (available from SynQuest Laboratories,
Inc.), was used as a dry etching gas with all other conditions
remaining the same. Etching rate and selectivity ratio were
evaluated in the same manner as in Example 1. The results are shown
in Table 1.

As seen from Table 1, when perfluoropropene was used as an
etching gas, a resist film for an ArF excima-laser tends to be etched,
and the selectivity ratio in etching is very small.

Example 5

Ten parts of a terpolymer comprised of 2,2,2-trifluoroethyl
methacrylate units, 2-ethyladamantyl methacrylate units and
t-butyl methacrylate units (copolymerization ratio: 0.4:0.35:0.25
by mole; molecular weight: 8,700) and 0.15 part of
triphenylsulfonium trifluoromethane sulfonate as an acid generator
were dissolved in 70 parts of propylene glycol monomethyl ether
acetate, and the resulting solution was filtered through a filter
having a pore diameter of 100 nm to give a resist solution.

A silicon substrate of an 8 inch diameter having a coating
of silicon oxide film with a thickness of 2 μm was coated with the
above-mentioned resist solution by a spin-coating procedure, and
then, the thus-coated substrate was pre-baked at 120°C on a hot
plate to form a resist film having a thickness of 300 nm. The resist
film was exposed to light through a mask pattern by an X-ray aligner.
The X-ray-exposed resist film was post-baked at 130°C, and then
subjected to a developing treatment at 25°C for 60 seconds with
an aqueous solution of tetramethylammonium hydroxide having a
concentration of 2.38% by weight, and dried to form contact holes
having a diameter of 100 nm.

The thus-obtained substrate having contact holes was set in

an ICP plasma etching apparatus. The inside of the apparatus was vacuumed, and perfluoro-2-pentyne as a dry etching gas, produced in Example 6, mentioned below, was introduced into the etching apparatus at a rate of 50 sccm. Etching was carried out at a plasma density of 10^{11} ions/cm^3 while the inner pressure was maintained at 0.67 Pa. Etching rate and selectivity ratio were evaluated in the same manner as in Example 1.

The results obtained in Examples 1 to 5 and Comparative Example 1 are shown in Table 1.

Table 1

Examples	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Com.Ex.1	Ex. 5
Resist	for ArF laser					for X—ray
Dry etching gas	A	B	C	D	E	A
Etching rate						
Silicon oxide film						
Central portion	621.0	593.5	518.4	521.2	500.9	550.1
Edge portion	564.1	520.4	410.2	415.4	468.9	516.2
Resist						
Central portion	33.6	42.1	43.9	43.4	156.5	44.7
Edge portion	41.5	56.6	65.1	63.9	426.3	51.1
Selectivity						
Central portion	18.5	14.1	11.8	12.0	3.2	12.3
Edge portion	13.6	9.2	6.3	6.5	1.1	10.1

Dry etching gas   A: Perfluoro—2—pentyne
                           B: Perfluoro—2—butyne
                           C: Perfluoro—2—pentene
                           D: Perfluoro—1,3—butadiene
                           E: Perfluoropropene
Etching rate, unit: nm/min
Selectivity ratio: (etching rate for silicon oxide film)/(etching rate for resist)

As seen from Table 1, in the case when a resist pattern is formed by irradiation with an ArF excima laser and the resist is dry-etched using perfluor-2-pentyne, perfluoro-2-butyne, perfluoro-2-pentene or perfluoro-1,3-butadiene (Examples 1 to 4), the etching rate for silicon oxide film is high and the selectivity ratio is large, as compared with the case when dry etching is carried

out by using perfluoropropene as a dry etching gas (Comparative
Example 1). In the case when a resist pattern is formed by X-ray
irradiation, and the resist is dry-etched using perfluor-2-pentyne
(Example 5), the etching rate for silicon oxide film is high and
the selectivity ratio is large.

Example 6 (Synthesis of perfluoro-2-pentyne)

A round glass flask equipped with a cooling tube was charged
with 140 parts of dimethylformamide. The flask was cooled to -50°C,
and pentafluoropropionaldehyde was blown into the
dimethylformamide to prepare a solution of
pentafluoropropionaldehyde in dimethylformamide. The
pentafluoropropionaldehyde used was prepared by heating 12.8 parts
of pentafluoropropionaldehyde hydrate (available from Central
Yakuhin K.K.) together with phosphorus(V) oxide whereby the
pentafluoropropionaldehyde hydrate was dehydrated. To the
solution of pentafluoropropionaldehyde, 37.5 parts of
1,1,1-trichloro-2,2,2-trifluoroethane (available from Tokyo
Kasei Kogyou K.K.) and 39.2 parts of zinc powder, previously
activated with acetic anhydride, were added at 0°C. The
thus-obtained reaction mixture was further stirred at 0°C for 30
minutes, and then, a reaction was carried out at 50°C for 4 hours.
Then the reaction mixture was cooled to room temperature, and 300
parts of water was added. The aqueous mixture was extracted with
107 parts of diethyl ether. This extraction was repeated twice
using the same amount of diethyl ether.

The thus-obtained liquid extract was dried over sodium
sulfate. The dried product was distilled to remove ether to give
36 parts of a crude product. GC-MS analysis of the crude product
revealed that 2-chloro-1,1,1,4,4,5,5,5-octafluoro-2-pentene was
produced. A Hastelloy autoclave was charged with 23.9 parts of
commercially available palletized potassium hydroxide having a
purity of 85% by weight and 36 parts of the above-mentioned 2-chloro-
1,1,1,4,4,5,5,5-octafluoro-2-pentene. The content was
thoroughly stirred and a reaction was carried out at 200°C for 6
hours.

The autoclave was cooled, and the reaction mixture was

distilled out. A trap for collection and a vacuum pump were connected, and the reaction mixture was collected at a subatmospheric pressure in the trap, cooled by liquid nitrogen, to give 3.7 parts of a reaction product.

The above-mentioned reaction procedures were repeated to collect the reaction products. 120 parts of the collected reaction products were distilled by the same procedures as in Production Example 1 to give 97.2 parts of perfluoro-2-pentyne fraction (boiling point: 5°C) having a purity of 99.9% by volume.

Industrial Applicability
According to the dry etching method of the present invention, a high etching rate and a high etching selectivity can be attained and a fine resist pattern can be formed with good stability on a silicon substrate, even for a resist having poor resistance to dry etching using a light source with a short wavelength of 195 nm or less.

Therefore, the dry etching method of the present invention is beneficially adopted for the production of semiconductor devices having integrated circuits of high integration and high performance such as VLSI (very large scale integrated circuit) and ULSI (ultra large scale integrated circuit).

According to the process for producing perfluoro-2-pentyne of the present invention, perfluoro-2-pentyne having a high purity can be easily produced from a readily available raw material.